

EVALUATION OF CARBON ANODES FOR RECHARGEABLE LITHIUM CELLS

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ABSTRACT

Both liquid phase intercalation technique and electrochemical intercalation technique were examined for the Li-carbon material preparation. The electrochemical techniques include a intermittent discharge method and a two step method. These two electrochemical techniques can ensure to achieve the maximum reversible Li capacity for common commercially available carbon materials. The carbon materials evaluated by two step intercalation method includes: pitch coke, petroleum coke, PAN fiber and graphite, materials. Their reversible Li capacity were determined and compared. In this paper, we also demonstrated the importance of EPDM binder composition in the carbon electrode. Our results indicated that it can impact the Li intercalation and de-intercalation capacity in carbon materials. Finally, two possibilities that may help explain the capacity degradation during the practical cell cycling were proposed.

INTRODUCTION

Rechargeable lithium cells containing lithium foil anodes are reported to have limited cycle life performance and safety problems. Both problems can be ascribed to the high reactivity of Li with the electrolyte and the formation of high surface area Li during cycling. To overcome these problems, the Li anode needs to be replaced by an alternate anode material which exhibits (1) low equivalent weight, (2) low voltage vs. Li, and (3) stability towards various electrolytes⁽¹⁾. At JPL, we have been evaluating alternate anode materials such as: Li-Al based alloy, Li-Mg₂Si and carbon materials. In this paper, we will focus on the evaluation of different types of carbon materials. Carbon has been studied⁽²⁾ as a candidate alternate anode material since it possesses the above mentioned properties. However, before it can be used as an anode for rechargeable lithium cells, the carbon material should be intercalated with Li.

Although carbon possesses the proposed properties, intercalation of Li into carbon is not trivial. Earlier studies did not deal with how to intercalate Li into carbon to achieve maximum theoretical capacity or specify the utilizable Li compositional region. The Li capacity and reversibility of carbon materials will be quite different depending on the raw material source and heat treatment history. In addition, fabrication of the carbon electrode is not trivial either since the carbon particles can not be compacted at room temperature into shapes without the addition of binders. Although at high temperature and pressure carbon can be compacted, the sintering makes the electrode less porous and changes the carbon surface properties. The optimum binder composition needs to be determined since too much binder will lead to lower specific energy, poor rate capability and inadequate Li

intercalation later, and insufficient binder can not hold the carbon particles together. Further, low porosity and nonuniform loading of carbon material in the electrode will also reduce the rate capability and intercalatable Li capacity. In this paper, we demonstrate techniques that will maximize reversible Li capacity in common commercially available carbon materials. This paper also includes a discussion of electrode fabrication and electrochemical studies on carbon materials.

EXPERIMENTAL

Two methods of Li-carbon material preparation were examined, i.e. the liquid phase intercalation and the electrochemical Li intercalation techniques. In the case of the liquid phase intercalation technique to prepare LiC_6 material, the preparation process was conducted in the argon-filled dry box with a Mo crucible as the molten Li container. Graphite rods were immersed into the molten Li at 350°C – 390°C for 8–10 hours and the final product was a golden-colored LiC_6 material.

On the other hand, the electrochemical intercalation of lithium into various carbon materials was studied using the following cell configuration: $(-) \text{Li} / 1.5 \text{M LiAsF}_6 \text{ in } 10\% \text{EC} + 90\% 2\text{-MeTHF} / \text{Li}_x\text{C} (+)$. The carbon materials were first evaluated for chemical stability and compatibility in the cell environment. The structure of the positive electrode materials were studied by x-ray diffraction method. The coulometric titration technique was applied to study the number of phases, phase composition, capacity and open circuit voltage (OCV vs. Li) of the materials. Electrodes were made by pressing and then formed by electrochemical intercalation with Li. The pressing technique was found suitable for the electrode fabrication. Ethylene propylene diene monomer (EPDM) was used as a binder. All electrodes were prepared by mixing the carbon powder with a solution of EPDM binder in cyclohexane until a uniform slurry was obtained. The slurry was spread on both sides of a nickel grid to form the electrodes. The electrodes were then pressed between a set of stainless steel plates. Typically, electrodes were coated with 10–15 mg of carbon per cm^2 , and were 10–15 mil thick. Electrochemical cells were constructed using these electrodes, lithium foil (Foose Mineral Corp.), porous polypropylene separators (Celgard no. 2400), and a 1.5 M solution of LiAsF_6 in a 10:90 mixture by volume of EC and 2-MeTHF. To describe a little more in detail, the electrodes were assembled using spiral wound cell configuration and then the cell stack is held by a glass vial with teflon mender in the center. The reason to use the glass vial is for the further evaluation of the cell components (post mortem analysis) after cycling experiment. The dc (terminal) voltage as a function of composition, cells were charged and discharged at constant current under ambient temperature conditions. Experiments were conducted in an oxygen and moisture free dry box.

RESULTS AND DISCUSSION

(1) Li_xC material preparation:

To examine the usefulness of the LiC_6 material prepared by the liquid phase intercalation technique, we evaluated its Li reversibility, the results indicated that about 0.08 Li per carbon is reversible at a slow rate (Figure 1). By comparison, we also evaluated the electrochemical Li intercalation into the same carbon materials. The results indicated that

Li_xC material prepared after intermittent discharge technique can have about 0.1 Li per carbon to be reversible at a higher rate. In view of this and for our own convenience of easy handling, the electrochemical intercalation technique was selected to prepare Li_xC material for this work.

(2) Electrochemical Li intercalation:

Before carbon material can be used as anode for rechargeable lithium cells, it should be intercalated with Li. A technique of intercalating Li repetitively at constant current (intermittent discharge technique) was tried. Initially, the voltage of the carbon electrode approaches zero volt vs. Li during the constant current discharge. At this point, it appears that the carbon electrode is no more useful; however, if the electrochemical intercalation process is repeated after the OCV goes above zero volt vs. Li, one can intercalate more Li into the carbon. After this stage, the Li intercalation into carbon material is possible. The results of the experiment are shown in Figure 2. In this experiment, we applied a constant current of 0.28 mA/cm^2 for the first discharge, the cell voltage precipitously came down to zero volt vs. Li, around the composition $\text{Li}_{0.0015}\text{C}$. At this point, we cut off the current and the cell voltage recovered to 1.6 V vs. Li. Now again, the carbon electrode was discharged at the same current density for the second time. As shown in Figure 1 that not only is the electrode kinetics improved but the lithium intercalation begins. Typically, Li can be put into carbon close to the maximum composition (LiC_6) after the fourth repeated discharge process. Figure 3 shows the voltage vs. composition relationship during the first Li intercalation ($I = 0.28 \text{ mA/cm}^2$) & de-intercalation ($I = 0.84 \text{ mA/cm}^2$) cycle in a 32 mAh cell. The results show a certain amount of intercalated Li is not recoverable during de-intercalation for the first cycle. However, during subsequent cycles, the amount of Li corresponding to the capacity of $0.05 < x \text{ in } \text{Li}_x\text{C} < 0.15$ can be reversibly cycled with negligible loss. Another intercalation technique is a two stages of Li reaction process, the first stage involves intercalating Li into carbon at higher current until the cell voltage is close to zero volt vs. Li, followed by the second stage of a smaller current lithium intercalation after the voltage recovers to a steady value. Our results showed that the maximum theoretical composition can be achieved in the second stage of Li intercalation. In addition, our results showed that the compositional region for the second stage is the real utilizable one.

(3) Evaluation of carbon materials:

The carbon materials that had been evaluated includes: pitch coke material, the same type of petroleum coke materials with different particle size, PAN carbon fiber and graphite materials. The coke materials that we have evaluated showed a typical powder x-ray diffraction pattern of broad peaks compared to the sharp and narrow peaks for graphite materials (Figure 4). Figure 5 shows the two step Li reaction of pitch coke material with initially high current, followed by a low current Li intercalation, it can have about 5070 of Li capacity (to be reversible). For the evaluation of petroleum coke materials, we examined the Li reversible capacity (by 1 V cut off) of the same petroleum coke materials but with different particle size. Figure 6 is for the one with larger particle size. The reversible Li capacity is about 0.06 Li per carbon. Similarly, the reversible Li capacity is also about 0.07 Li per carbon for the same coke material with smaller particle size (Figure 7). The major difference is that the irreversible Li capacity is much larger for the small particle size coke materials. This indicated that the surface of carbon material plays an important role in the electrochemical intercalation process. Also, we evaluated the reversible Li capacity in the PAN-based carbon fiber material. The results indicated that about 0.1 Li per carbon can be

reversibly cycled at a slow charge and discharge rate (Figure 8). For the case of graphite material, 0.124 Li per carbon can be reversibly cycled after a two step Li reaction (Figure 9). To make a comparison, we summarized the reversible Li capacity of different types of carbon materials in Table 1.

(4) Effect of binder composition:

From our TiS_2 studies, it was found that the TiS_2 cathode performance is influenced significantly by the binder composition. And similarly, the EPDM binder composition can also impact the intercalation of Li into carbon. In other words, either excess or inadequate amount of binder will degrade performance of carbon electrode. The electrochemical performance of the carbon electrode with 3.0 w% EPDM binder composition was studied as shown in Figure 10. The results indicated that the electrode composition corresponding to 3 w% EPDM exhibited very low Li intercalation capacity, and the further intercalation of Li is totally impossible even at a lower current ($I = 0.188 \text{ mA/cm}^2$). It can be concluded that the carbon electrode with 3 w% EPDM composition gives poor cell performance. On the other hand, lower binder concentration (2 w% EPDM) resulted in higher Li intercalation capacity. Similarly, the EPDM binder composition in the pitch coke electrode can also impact the intercalation of Li into this material. Most obviously, the reversible Li capacity is quite different when the different EPDM binder composition is used in the pitch coke electrodes. As shown in Figure 11, pitch coke electrode made with less binder yields significantly higher reversible Li capacity compared to that of electrode with higher binder composition. All of these results indicated that binder composition plays an important role in the carbon electrode fabrication.

(5) Rate capability of graphite evaluated:

In a 1 Ah capacity cell, the graphite material evaluated can have a C/20 discharge rate and C/3 charge rate and still maintains a capacity greater than 200 mAh/gm (Table II). As our understanding, the C/20 discharge rate is still slow for some special applications, therefore, the future studies will be focused on the improvement of the material's rate capability.

(6) Failure model of capacity decline:

Assessment of our cycling data yield a concern for certain types of graphite materials, the concern is a progressive increase in the amount of Li intercalation each cycle (Figure 12), and corresponding the depletion of Li supply. One of the possibility is that carbon particle break off which increase the surface area during cycling. The Li is gradually consumed to form film for the increased surface area. Another possibility is that it may be due to the continuous dissolution of the unstable film formed on the carbon material surface. These may help explain the capacity degradation in the real (practical) cell situation.

SUMMARY

Electrochemical techniques were developed for the incorporation of lithium into carbon up to the theoretical composition to ensure maximum reversible capacity. Typically, Li can be intercalated into carbon close to the maximum composition LiC_6 . And it was found that the maximum reversible Li capacity of Li-graphite material is about 75% of its theoretical capacity, and the maximum reversible Li capacity of Li-coke materials is about 50% its Li capacity. The results also indicated that the binder concentration in the carbon electrode can significantly affect the Li intercalation & de-intercalation capacity. And the capacity decline observed in the practical cell cycling may be due to the decrease of carbon particle

size with cycling and the continuous dissolution of surface film.

ACKNOWLEDGEMENTS

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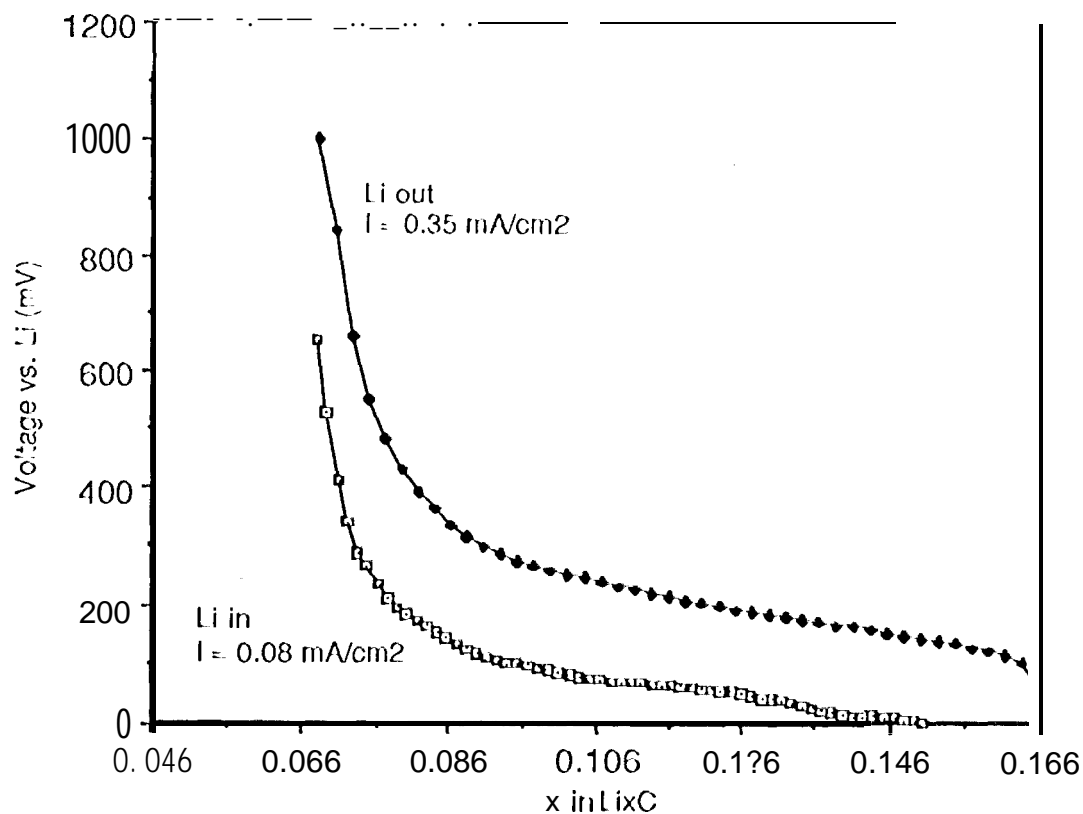


Figure 1. Li de-intercalation and intercalation in LiC_6 material prepared by the liquid phase intercalation technique.

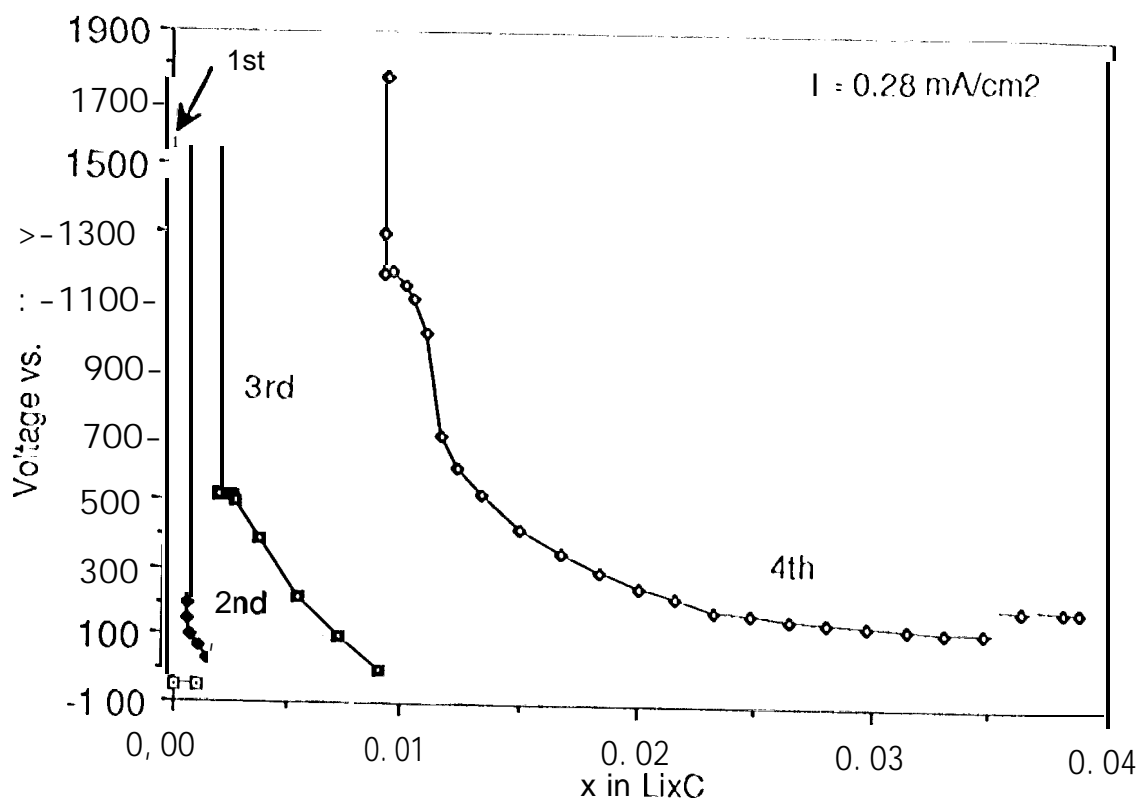


Figure 2. The improved discharge performance of Li intercalating into carbon using intermittent discharge technique.

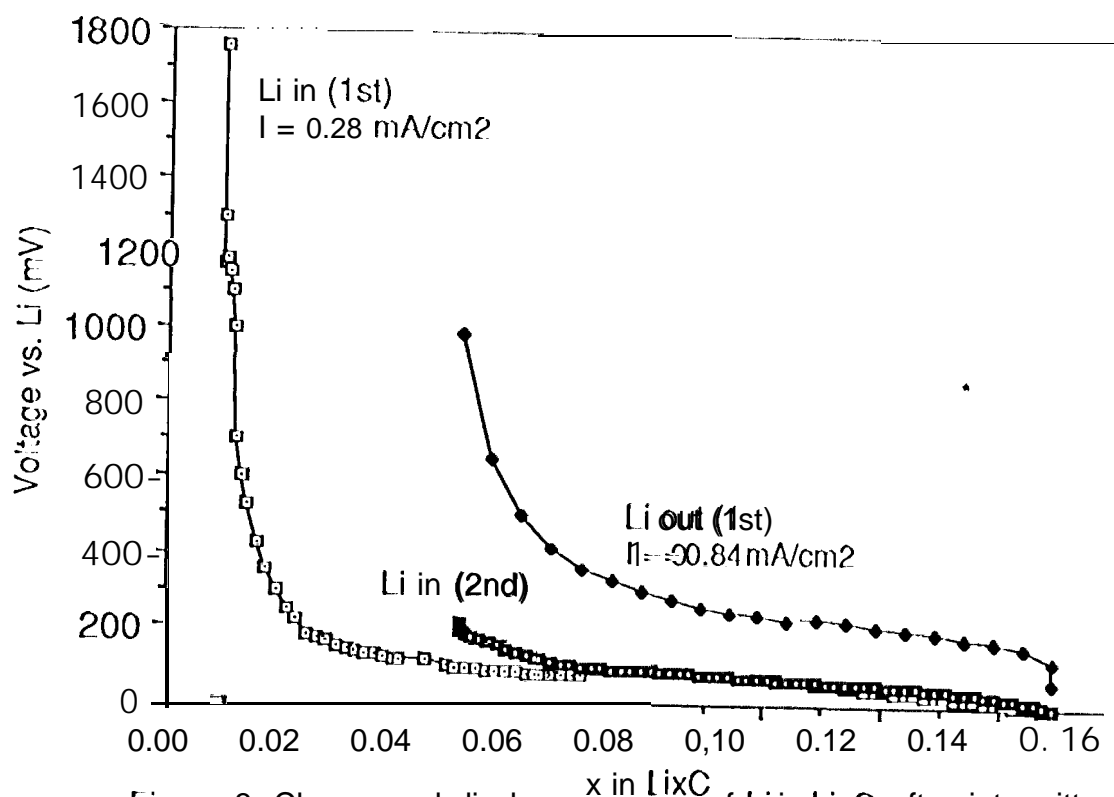


Figure 3. Charge and discharge curves of Li in Li_xC after intermittent discharge treatment.

X-RAY DIFFRACTION PATTERN

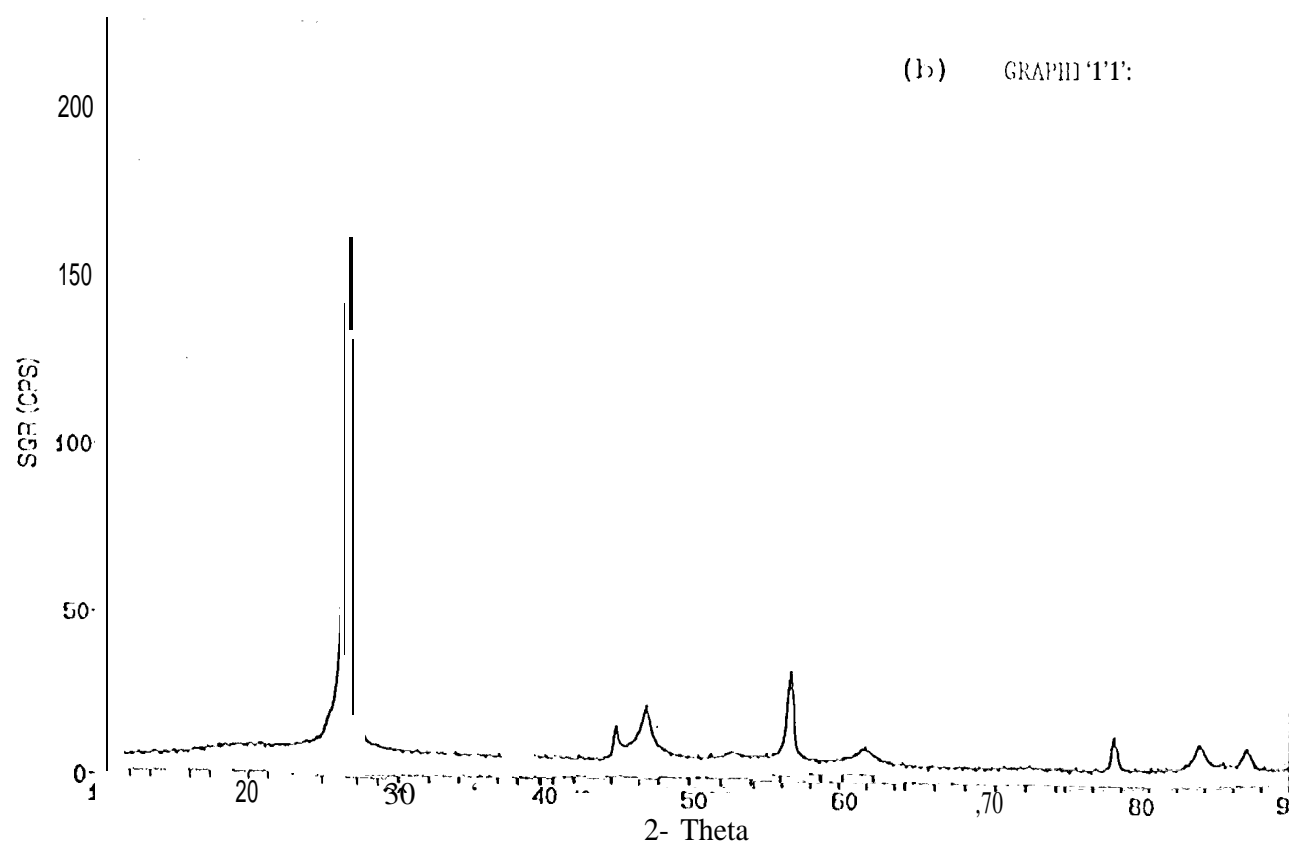
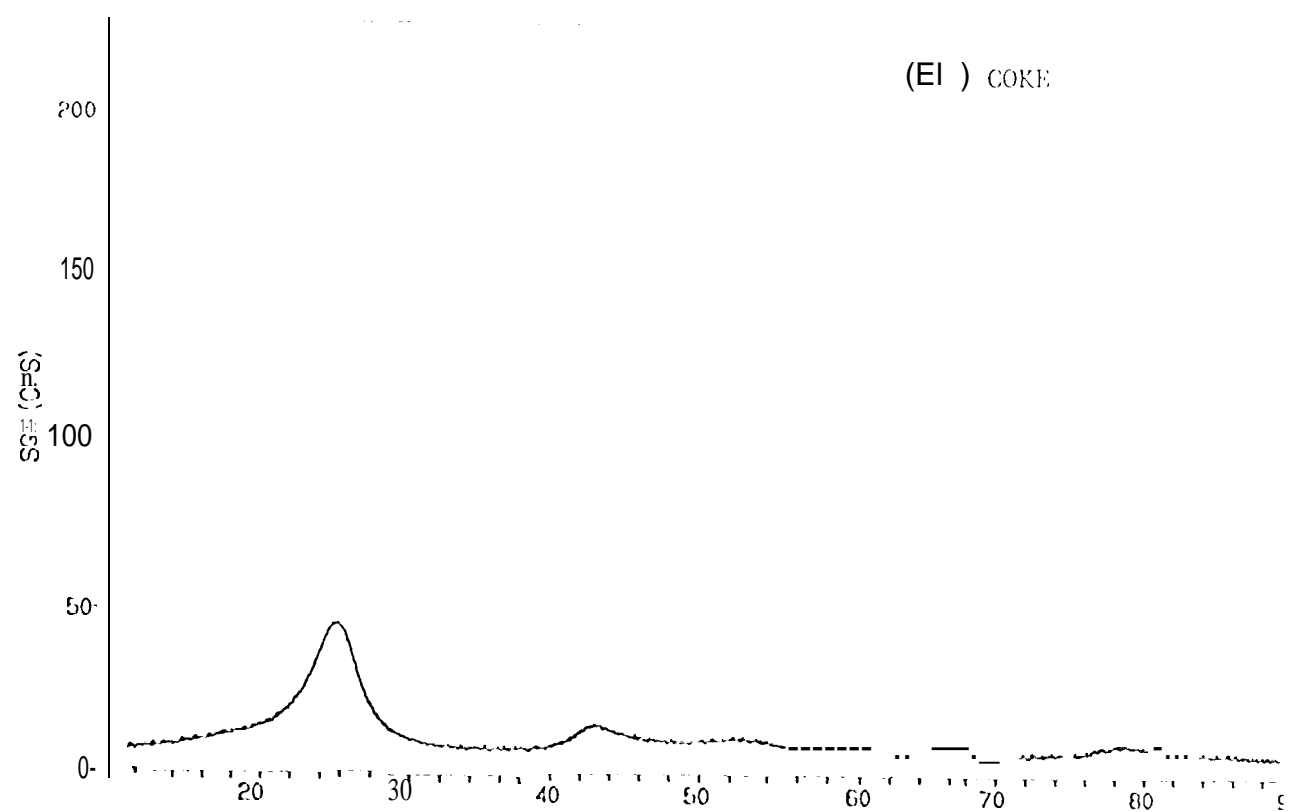


Figure 4. X-ray diffraction patterns of (a) coke (b) graphite.

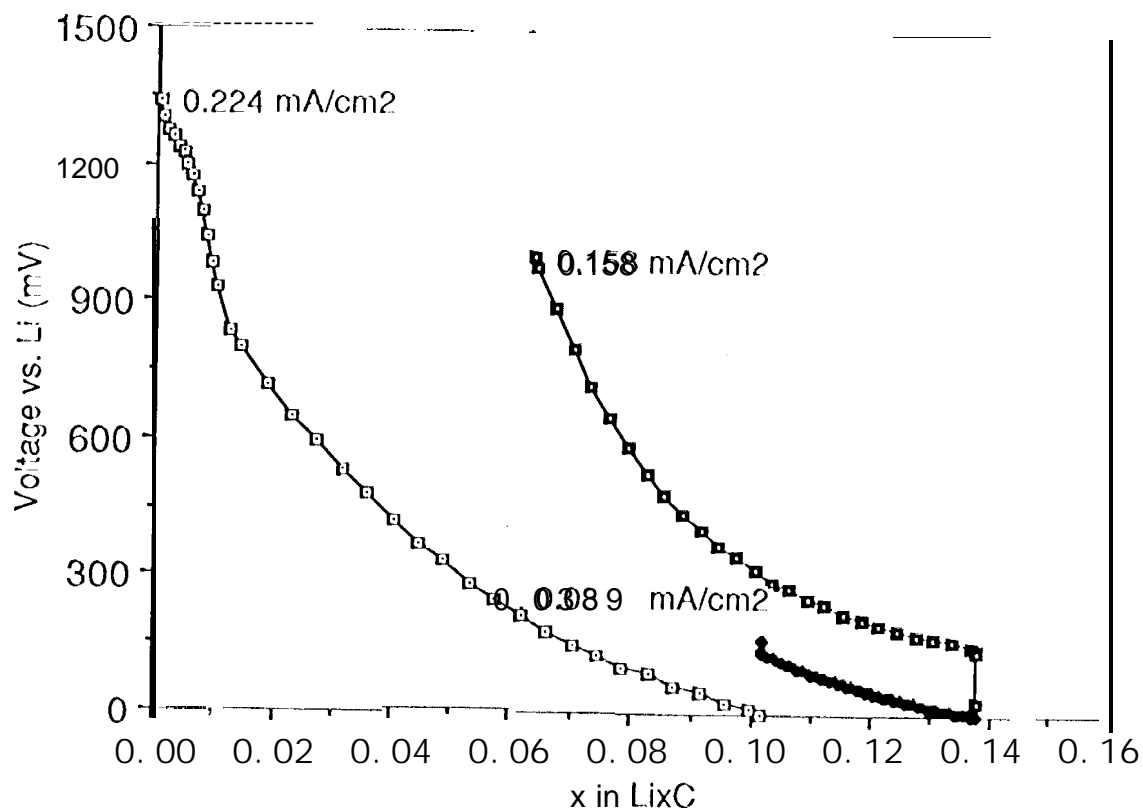


Figure 5. Electrochemical intercalation of Li into pitch coke by two steps.

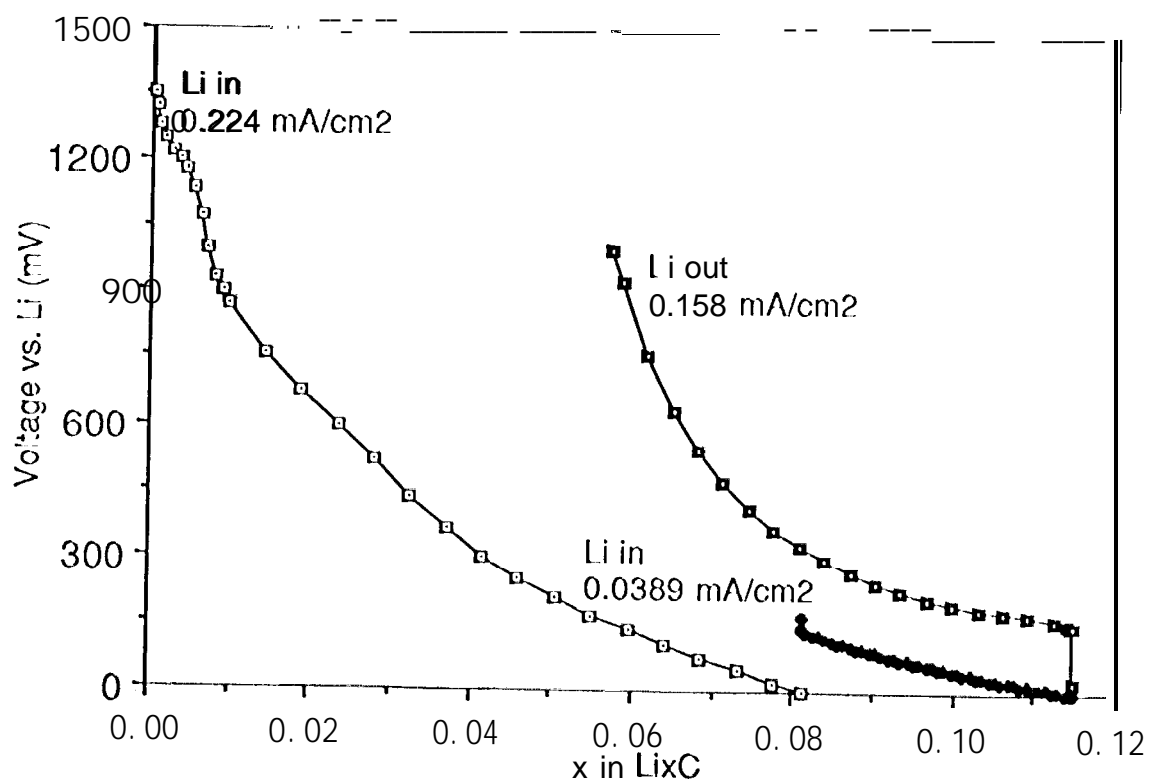


Figure 6. Electrochemical intercalation and de-intercalation in petroleum coke with large particle size.

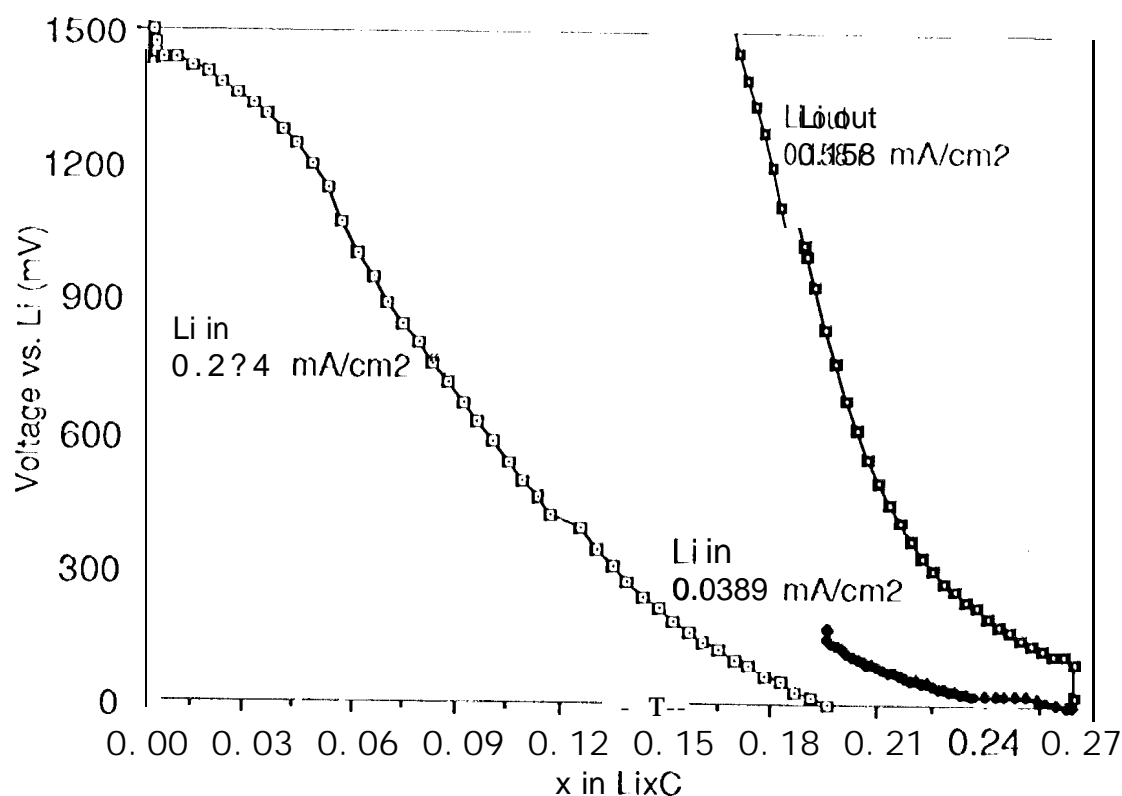


Figure 7. Electrochemical intercalation and de-intercalation of Li in petroleum coke with small particle size.

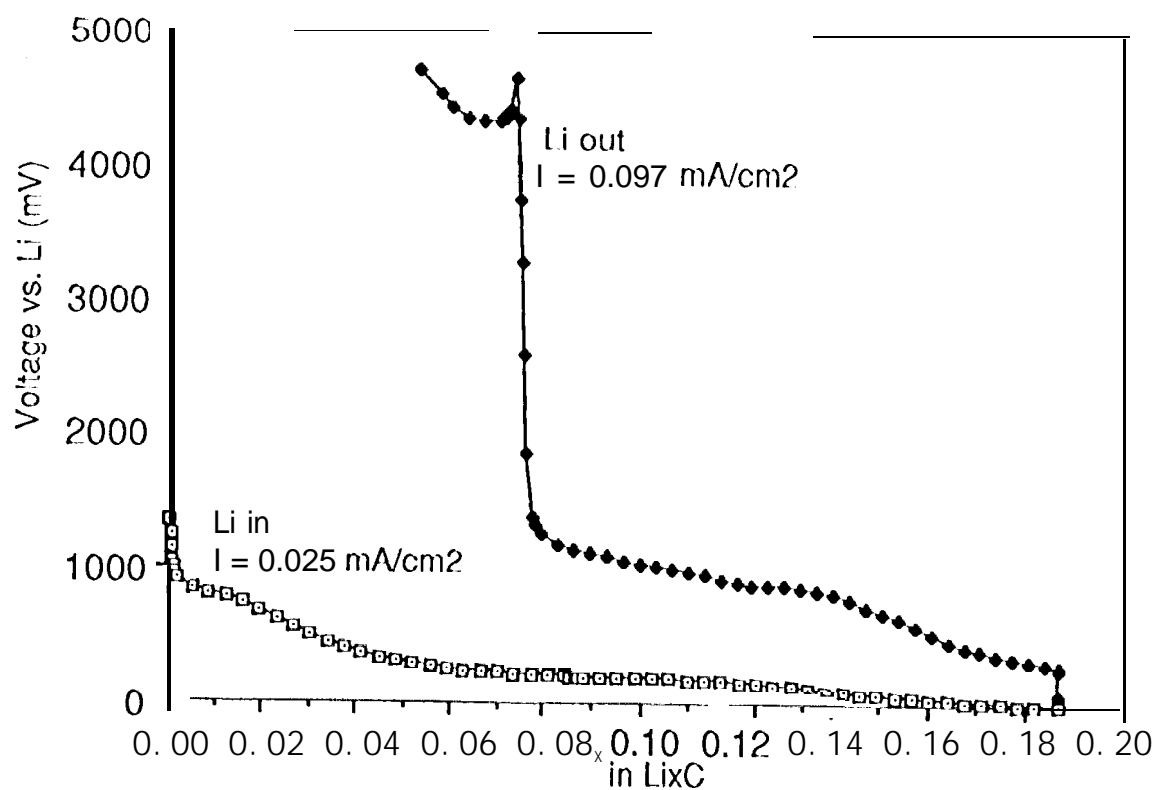


Figure 8. Electrochemical Li intercalation and de-intercalation in PAN-based carbon fiber.

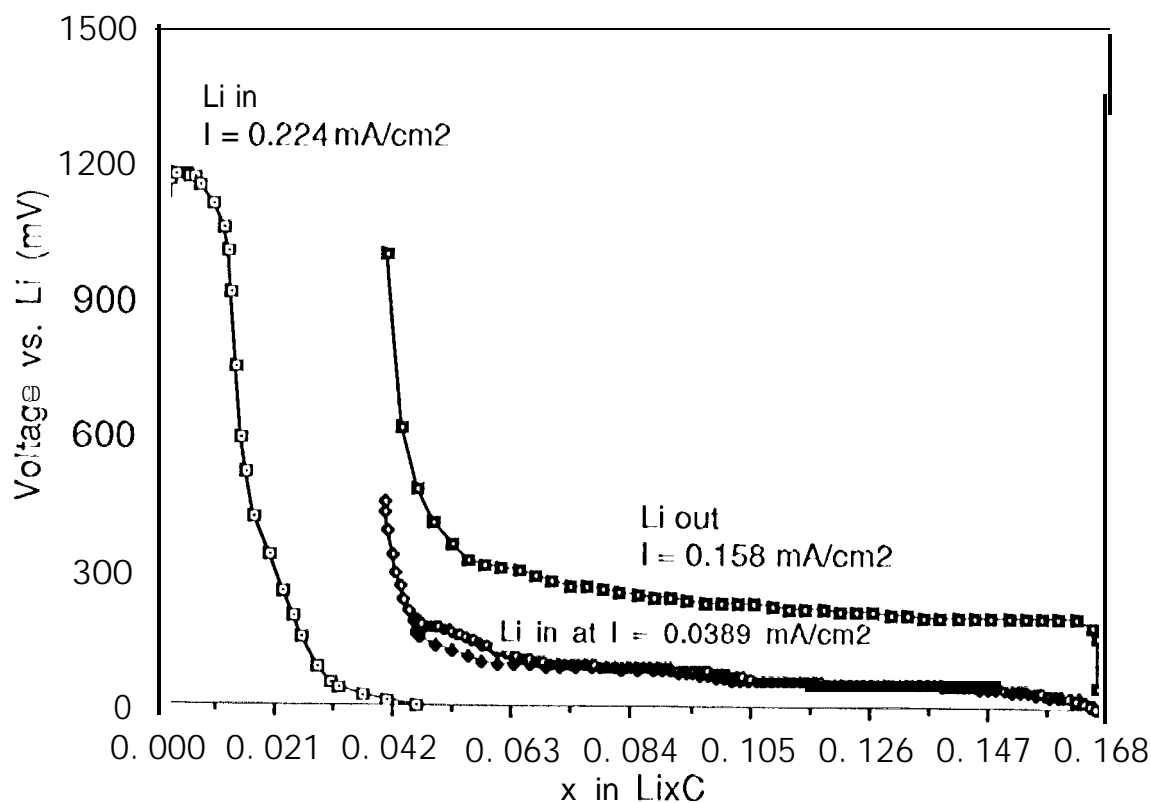


Figure 9. Electrochemical Li intercalation and de-intercalation in graphite.

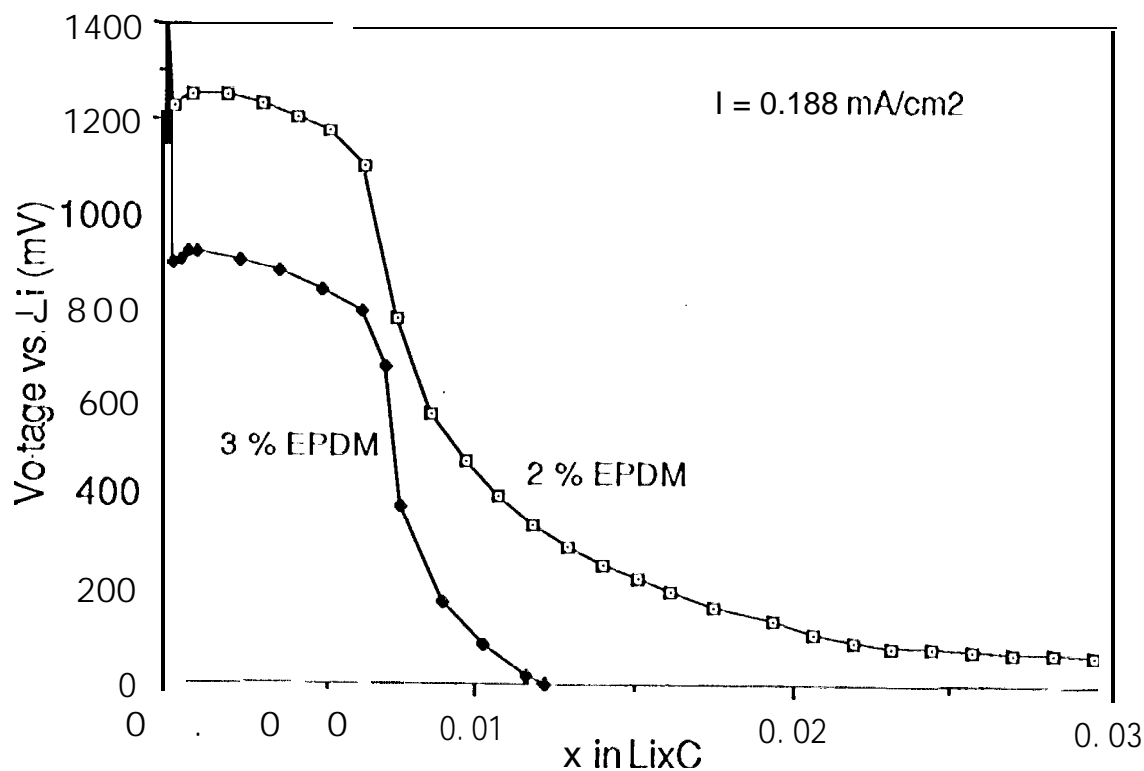


Figure 10. The effect of EPDM binder concentration on the electrochemical intercalation of Li into graphite.

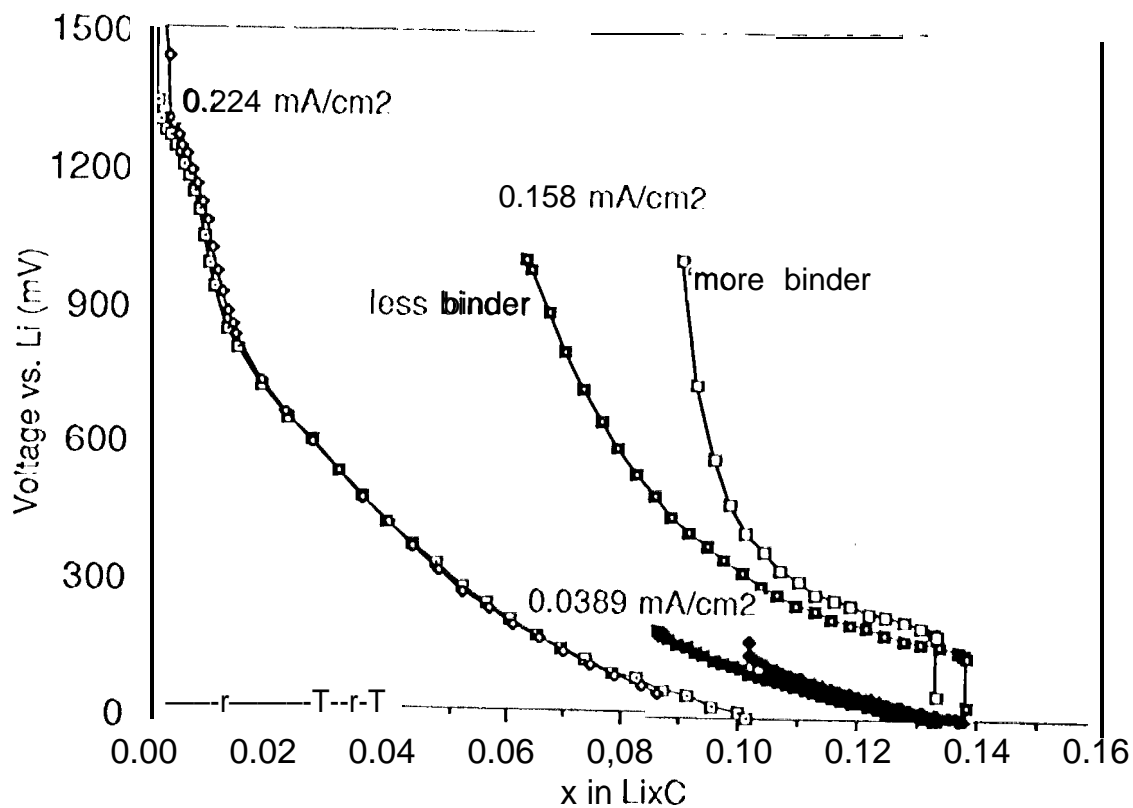


Figure 11. Effect of binder composition on the Li de-intercalation in pitch coke.

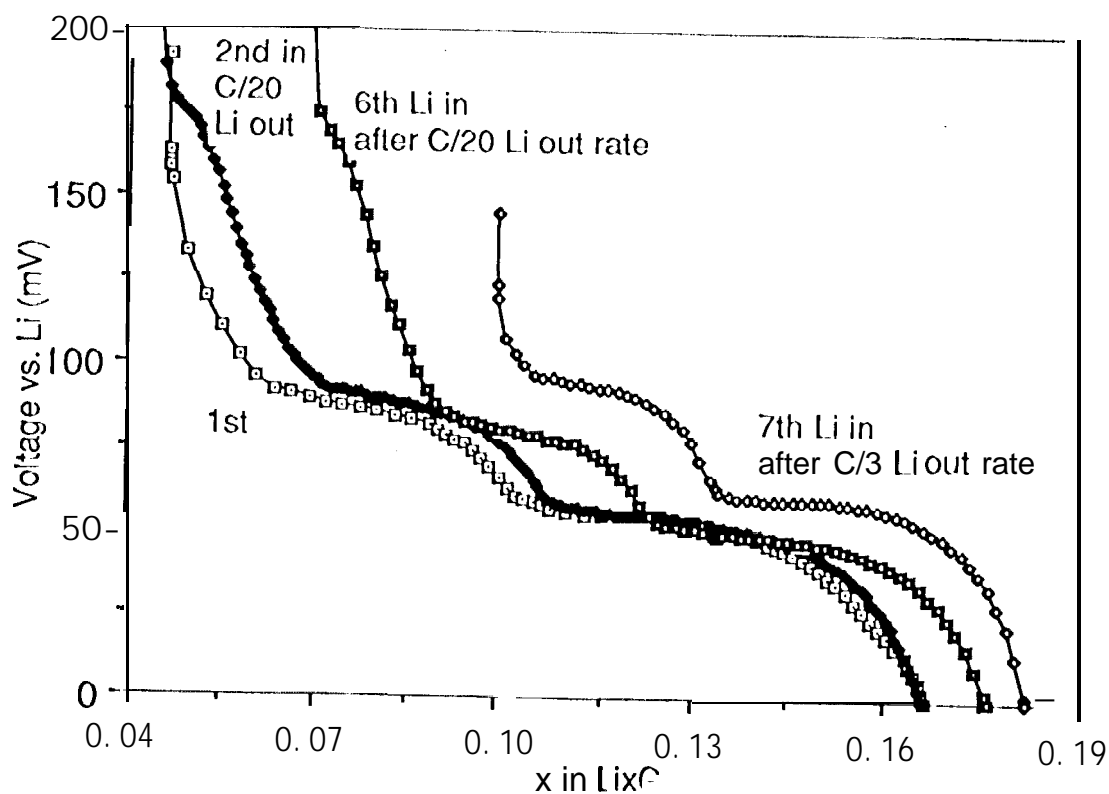


Figure 12. A progressive increase in the amount of Li intercalation each cycle in certain types of graphite materials.

TABLE I. The Comparison of Reversible Li Capacity of Carbon Materials Evaluated

(1) PITCH COKE :	0.070 Li PER CARBON
(2) PE1ROLEUM COKE:	0.057-0.077 Li PER CARBON
(3) PAN FIBER:	0.097 Li PER CARBON
(4) GRAPHITE:	0.124 Li PER CARBON

* PAN FIBER HAS VERY LOW RATE CAPABILITY.

TABLE II. Rate Capability of Li out (C) and Li in (D) in Li_xC Anode

CURRENT (mA)		CAPACITY (mAh)
D	26	783
c	50	789
D	26	791
c	100	763
D	50	728
c	50	741
D	50	734
c	100	716
D	50	714
c	200	697
D	50	710
C	300	670

* CAPACITY > 200 mAh/gm at 1 mA/cm².